

PATENT SPECIFICATION

50 JAN 1937



Convention Date (United States): Nov. 6, 1936.

497,694

Application Date (in United Kingdom): Nov. 5, 1937.

No. 30413/37.

Complete Specification Accepted: Dec. 23, 1938.

COMPLETE SPECIFICATION

Improvements in and relating to the Decomposition of Titanium Salt Solutions by Hydrolytic Precipitation

We, TITAN COMPANY INC., a Corporation organised under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, and having an office address at 111, Broadway, City, County and State of New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The invention relates to the production of titanium dioxide pigments by the hydrolytic precipitation of titanium salt solutions and the calcination of the precipitate.

In British Patent Specification No. 481,892 it is explained that titanium dioxide obtained by the calcination of the precipitate of a titanium salt solution may exist as the anatase modification (refractive index 2.55) or the rutile modification (refractive index 2.71). Further that the anatase modification may be obtained from titanium sulphate solutions and the rutile modification from titanium chloride solutions. In view of the higher refractive index of the rutile modification it would be desirable to employ titanium chloride solutions, but at the present day commercial production is confined almost entirely to the preparation of the anatase modification from sulphuric acid solutions, owing to the difficulty met on a commercial scale in obtaining precipitated particles of suitable form for pigment purposes from the titanium chloride solutions, the precipitate normally being in a very fine state of division and in consequence difficult to filter and impossible to wash free from impurities contained in the mother liquor. A large amount of work has been carried out on the preparation of titanium dioxide pigments from titanium salt solutions, and particular attention has been paid to the possibilities of obtaining products of suitable form from titanium chloride solutions. The result of the investigations has been a number

of suggestions, some of which have been adopted in practice, either to add to the solution materials which will assist the hydrolysis and influence the nature of the precipitate, or to effect the hydrolysis in the presence of suspended insoluble materials which influence the nature of the precipitate. British Specification No. 308,725 describes the hydrolytic precipitation of titanium compounds from mineral acid titaniferous solutions by adding the solution to a hot aqueous bath and in order to prevent aggregation an organic acid with or without phosphoric acid is dissolved in the hydrolysis liquor. No specific limits are given for the quantity of organic acid but a fairly large proportion is contemplated as the amount is compared with that required for a double decomposition reaction with the titanium content. As is described in Specification No. 481,892, whilst the acids have a dispersing action when used in the proportions described in No. 308,725, a very small quantity in a titanium chloride solution has the surprising effect of acting as an aggregation agent. British Specification No. 433,960 describes a process in which hydrolysis of a titanium salt solution is effected in the presence of a small amount of a finely dispersed titanium salt which is difficultly soluble in dilute mineral acids. Examples of such salts are titanium phosphate, titanium potassium sulphate and titanium potassium fluoride. These salts provide "nuclei" for facilitating the precipitation.

The process described and claimed in Specification No. 481,892 already referred to above is a process for the production of titanium dioxide having the rutile crystalline structure comprising hydrolysing an aqueous solution of titanium tetrachloride and calcining the precipitate wherein the hydrolytic precipitation is effected in the presence of negative divalent ions derived from a substance added to the solution in a proportion not exceeding 0.1 mol. to each mol. titanium reckoned as TiO_2 present in the hydrolysis

[Price 1/-]

solution, and wherein the hydrolytic precipitation is effected in the absence of any added insoluble material suspended in the solution.

- 5 It has now been found that the same desirable results, namely, the production of titanium dioxide having the rutile crystalline structure in a suitable form as regards particle size, can be obtained by
10 the hydrolytic precipitation of an aqueous solution of titanium tetrachloride in the presence of other negative polyvalent ions, that is ions having a valency of three or more. Furthermore, it has
15 been found that the same desirable results may be obtained by the hydrolytic precipitation of aqueous solutions of titanium fluorides and complex titanium fluorine compounds in the presence of
20 negative ions having a valency of two or more. In both cases the substance from which the negative polyvalent ions are derived is added in very small quantities, namely, not more than 0.01 mol of the
25 substance to each mol of titanium reckoned as TiO_2 present in the solution. The present invention accordingly comprises a process for the production of titanium dioxide having the rutile
30 crystalline structure comprising hydrolytically precipitating an aqueous solution of titanium tetrachloride, of titanium fluoride or of a complex titanium fluorine compound and calcin-
35 ing the precipitate wherein, in order to obtain an easily filtrable hydrated titanium compound the hydrolytic precipitation is effected in the presence of a small amount of a negative polyvalent
40 ion which, with a titanium fluoride or complex titanium fluorine solution, has a valency of two or more and, with a titanium tetrachloride solution, has a valency of three or more, the substance
45 from which the negative polyvalent ion is derived being present in an amount not greater than 0.01 mol of the substance to each mol of titanium reckoned as TiO_2 .
50 The negative polyvalent ions employed may be ions of inorganic acids and of ionisable organic acids. For example divalent ions, the use of which is only claimed in the present application in con-
55 nection with solutions of titanium fluoride and complex titanium fluorine compounds since the use of such ions in conjunction with titanium tetrachloride solutions is claimed in Specification No.
60 481,892, may be obtained by the addition to the hydrolysis solution of sulphuric, arsenic, carbonic, oxalic or tartaric acid or one of their alkali metal salts. Tri-
65 valent ions, the use of which is claimed in the present application both in con-

nection with tetrachloride, titanium fluorides and complex titanium fluorine compounds, may for example be obtained by the addition of phosphoric or citric acid or a soluble alkali metal phosphate
70 or citrate. More specific examples of salts which may be employed to give the negative ions are sodium sulphate, ammonium oxalate, lithium carbonate, sodium arsenate, sodium citrate and
75 potassium tartrate. A solution containing the ion may be added to the titanium solution, or alternatively the titanium solution may be added to the solution containing the ion. Conveniently the
80 acid or salt is dissolved in a large volume of water, the temperature is then raised and the titanium solution added.

Only a small amount of the polyvalent ion is required, to obtain the desired result, and as the polyvalent negative ions have a tendency to associate themselves, for example by adsorption, with the particles of hydrated titanium dioxide and they are not removed by washing, this effect being particularly noticeable with the sulphate and phosphate ions, the amount of polyvalent ion employed must not be so great as to contaminate un-
85 desirably the hydrated titanium dioxide.

The titanium solution is preferably relatively concentrated containing approximately 15% of titanium calculated as TiO_2 , and it should be substantially free from impurities. Such solutions give
90 optimum results, but no particular concentration of titanium nor any particular condition of purity of the solution is essential for the successful carrying out of the process of the invention.

The term "titanium fluorides and complex titanium fluorine compounds" is used broadly in this specification and in the claims to include not only titanium tetrafluoride but also complex
95 fluorides of titanium, for example amino titanium tetrafluorides, $TiF_4 \cdot xNH_3$, and those compounds of titanium which are sometimes regarded as the double fluorides of titanium and other elements or
100 radicals, for example $TiF_4 \cdot xNH_4F$, as well as combinations of such compounds for example $TiF_4 \cdot xNH_3 \cdot yNH_4F$.

The desirable effects obtained by using the polyvalent ions in accordance with
105 the present invention are obtained regardless of the exact method adopted for hydrolytically precipitating the hydrated titanium dioxide from the titanium solution; for example, the hydrated titanium
110 dioxide may be hydrolytically precipitated in the well known manner by raising the temperature of the solution to, or approaching, the boiling point which
115 step may or may not be accompanied by

70

75

80

85

90

95

100

105

110

115

120

125

130

a dilution of the titanium solution.

The hydrolytic precipitation is preferably carried out under such conditions as to give relatively rapid precipitation. It is found that the presence of the polyvalent negative ions has the effect of preventing the precipitated particles assuming an extremely fine form so that the particles obtained are of a suitable size for pigment purposes. The precipitate is thus readily filterable and easily washed. Furthermore, the precipitate when calcined gives a product having the rutile crystalline structure and having a remarkably high hiding power and tinting strength.

The process of the present invention is illustrated by the following specific Examples:—

EXAMPLE 1.

Titanium tetrachloride is dissolved in cold water to give a clear aqueous solution of titanium containing about 15 per cent. of titanium reckoned as TiO_2 . All the iron present is reduced to the ferrous condition in order to prevent the hydrolysis which ferric salts readily undergo. In order to ensure the absence of ferric iron throughout the precipitation it is preferable to reduce the solution to a content of two to three grams per litre of trivalent titanium reckoned as TiO_2 . 1000 kilos of the chloride solution containing 15 per cent. titanium reckoned as TiO_2 are added to 7000 litres of boiling water containing two kilos of citric acid, during about one hour. When the addition has been completed about 95 per cent. of the titanium will have been precipitated as hydrated titanium dioxide; the latter is in a coagulated form such that it settles well and may be readily filtered and washed. After filtration and washing the precipitate is calcined at a temperature of from 700 to 1000° C.

EXAMPLE 2.

Ilmenite is furnace with ammonium fluoride and the vapours of diamino tetrafluoride $TiF_4 \cdot 2NH_3$, are collected. The tetrafluoride compound is dissolved in water containing sodium sulphate, the necessary quantities being used to obtain a solution containing about ten per cent. by weight of titanium reckoned as TiO_2 and 0.05 per cent. by weight of sulphate

radical. The solution is then boiled to precipitate hydrated titanium dioxide in a filterable condition. The precipitate is washed and calcined.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of titanium dioxide having the rutile crystalline structure comprising hydrolytically precipitating an aqueous solution of titanium tetrachloride, of titanium fluoride or of a complex titanium fluorine compound and calcining the precipitate wherein in order to obtain an easily filterable hydrated titanium compound, the hydrolytic precipitation is effected in the presence of a small amount of a negative polyvalent ion which, with a titanium fluoride or complex titanium fluorine solution, has a valency of two or more and, with a titanium tetrachloride solution, has a valency of three or more, the substance from which the negative polyvalent ion is derived being present in an amount not greater than 0.01 mol of the substance to each mol of titanium reckoned as TiO_2 .

2. A process as claimed in Claim 1 wherein the polyvalent ion is obtained by the addition of phosphoric or citric acid or an alkali metal phosphate or citrate to the solution.

3. A process as claimed in Claim 1 wherein a fluoride solution is employed and the polyvalent ion is obtained by adding oxalic, tartaric, sulphuric, arsenic or carbonic acid or one of their alkali metal salts to the solution.

4. A process as claimed in any one of the preceding Claims carried out substantially in the manner hereinbefore described.

5. Calcined titanium dioxide having the rutile structure when obtained by the process claimed in any one of the preceding claims.

Dated this 5th day of November, 1937.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London,
E.C.1,

Chartered Patent Agents.